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FINAL TECHNICAL REPORT ON ONR CONTRACT (N00014-88-K-0413)

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Final Report (ONR)

Outline

I. Introduction

The following is a Final Report to the Office of Naval Research (ONR) for work performed at the University of Hawaii in the Department of Physics and Astronomy under the supervision of Dr. James R. Gaines. The contract (N00014-88-K-0413) began on July 1, 1988 and terminated Nov. 30, 1990. In all $123,589 in ONR funds were expended over the twenty-nine months of the contract.

In addition to Dr. Gaines, Dr. P.P. Crooker, Professor of Physics, Dr. Yi Song, Postdoctoral Fellow, and Mr. Anupam Misra all devoted time to this contract at some time during its tenure. Mr. Misra's Ph. D. thesis will be based in part on the measurements supported by this contract although financial support for Mr. Misra ended before he completed his dissertation work. One collaborative effort of note was the one with Mr. Albert H. Cardona of Superconductor Technologies, Inc. (Santa Barbara, California), who supplied Thallium films for one of our studies. One publication (number 6 on the list) resulted from this collaboration. In all, during the course of this contract, six papers were published in refereed journals, with a seventh manuscript being prepared for submission.

The major thrust of this contract was to investigate the electrical noise power generated by high temperature superconductors in the temperature region just above their superconducting transition temperature. Previous measurements by Gaines and Song while at Ohio State University had shown that for bulk superconducting samples the noise power peaked in the transition region, just where bolometer type detectors would be most sensitive.

The ONR contract permitted this work to be continued when Dr. Gaines moved from Ohio State to the University of Hawaii. As a result of the work supported by this contract, there are now much more systematic measurements of the 1/f noise power in high T_c superconductors--including bulk samples, composites of normal metals and high T_c materials, thin films, and single crystals. The thin film samples were supplied by companies but all other samples were made in our laboratory. Two significant findings have resulted from this contract:

(1) Our most recent work on single crystals tentatively identifies the source of the anomalous 1/f noise peaks in the superconducting transition region and points out how this problem can be avoided in device applications. *The source of the anomalous noise peak is the freezing (or melting) of the vortex lattice.*

(2) Our earlier work produced a qualitative model of the enhanced 1/f noise in the normal state based on metal-insulator-metal contacts. The model is capable of a quantitative prediction if several parameters used to fit data could be measured independently. *The source of the large 1/f noise is the poor contact between grains or at twin boundaries.*

> *Thus we have provided answers to two of the most important questions posed by our first measurements of 1/f noise in high T_c materials: What is the source of the enhanced 1/f noise in the normal state? Why is there a peak in the 1/f noise in the superconducting transition region?*

The report is organized into the following sections: II. Apparatus construction and 1/f noise measurement procedures; III. Sample fabrication and characterization; IV. Experimental results on 1/f noise; V. Model calculations; and VI. Conclusions. The publications resulting from this contract are listed in the Appendix.

II. Apparatus construction and 1/f noise measurement procedures

II.A. Initial setup

The initial activities supported by the ONR were devoted to setup and testing of apparatus for sensitive 1/f noise measurements. In terms of the apparatus, all the necessary equipment for making electrical noise measurements using the cross-correlation technique was purchased and assembled. We completed the tests of this equipment and then used it extensively for our 1/f noise experiments.

In order to improve our ability to detect the noise power spectrum, we made two improvements: (1) we purchased a spectrum analyzer that permitted us to measure to a lower frequency of 100 microhertz; and (2)

we used the "cross-correlation" method to measure the noise. To employ this technique, we purchased a second "signal track" consisting of a transformer, low pass/high pass filter, and a low noise preamplifier. The signal from the sample resistor is sent tnrough both tracks and then into the spectrum analyzer. Since noise picked up in the amplifier chains is "uncorrelated", the only noise present after correlation in the spectrum analyzer comes from the sample. This eliminates amplifier noise, which becomes appreciable below 1 Hz. The improvement is illustrated as follows: (1) we have a sensitivity in measuring S_V/V^2 higher than 10^{-16} s^{-1} for the cross-correlation technique. In contrast, with only one signal channel, the spectrum is distorted by the preamplifier noise and has more than an order of magnitude lower sensitivity, worse than 10^{-15} s^{-1}. (2) the minimum frequency we can use is 0.04 Hz instead of 1 Hz, our lower frequency when the single channel is used. This technique represented a great improvement over our earlier one and allowed us to take better quality data.

II.B. 1/f noise measurement procedures

The noise power is measured from 0.1 Hz to 100 Hz by a dc four probe cross correlation method. A battery generated dc current (maximum 260 mA) is passed through a sample in series with a large ballast resistor (typically 100 Ω, thus at least 1000 times larger than the sample resistance). The voltage across the sample is dc filtered through a large capacitor (1.0 F capacitance) and then split into two (identical) parallel branches. In each branch the voltage signal is fed into a low noise transformer followed by a low noise preamplifier. The cross correlation spectrum is measured by an HP3562A dynamic signal analyzer which detected signals from the two parallel preamplifiers. The "cross-correlation spectrum" is calculated by performing rms averages of Fast-Fourier Transforms (FFT's) of the input time dependent signals from one branch multiplied by the complex conjugate of the Fast-Fourier Transforms from the other branch.

The sample is loaded in a small cryostat cooled by liquid nitrogen and the temperature was adjusted manually by a battery driven dc heater. Commercial temperature regulators produce too much noise. The electronics (except for the HP3562A analyzer) and the cryostat are kept

inside a double walled metal box and batteries are used to supply power for the components inside the box.

The background noise which is essentially the amplifier noise plus the sample thermal noise is determined by measuring the noise power spectrum of a pure copper wire with the same resistance as our $Tl_2Ba_2Ca_2Cu_3O_{10}$ sample. The noise power from the copper wire is so small that no 1/f behavior is observed as the noise power spectrum is frequency independent. The excess noise in the sample is thus obtained by subtracting the background noise from the total measured noise.

To check on the contribution made by contact noise, we increase the ballast resistance and the driving current both by a factor of 2 so that the voltage across the sample remained constant but the ratio of ballast resistance to sample resistance is doubled. We have not observed any change in either the slope or the magnitude of the noise power spectrum, indicating that the contribution from the contact noise is negligible. We also performed a series of measurements in which we keep the ballast resistance at a constant value but we systematically increase the driving current (up to 260 mA) so that the voltage across the sample is accordingly increased. The resulting noise power spectrum is enhanced and we are able to fit the magnitude of the noise power to a V^2 dependence where V is the voltage across the sample. This result assured us that there is no self-heating in the sample during the measurement which, if it existed, would lead to a V^3 dependence.

III. Sample fabrication and characterization

III.A. Fabrication and testing of $Y_1Ba_2Cu_3O_{7-\delta}$ + Cu + Ag composites

We have fabricated a new series of superconducting composites with T_c well above the liquid nitrogen temperature. Powders of $Y_1Ba_2Cu_3O_{7-\delta}$ (prepared in advance using the standard solid state reaction method), metallic copper (Cu), and metallic silver (Ag) were thoroughly mixed together according to a predetermined stoichiometry. The mixture was pressed into pellets for final sintering in two steps. In the first step, pressed pellets were sintered in flowing nitrogen gas for 2 hours followed by slow cooling to 200°C. The sintering temperature was chosen to be

790°C, the eutectic point of a silver-copper system. In the second step, the pellets were sintered at 900°C in flowing oxygen gas for 2 hours and slowly cooled to 500°C. An additional annealing at 500°C in flowing oxygen gas for 6 hours was used. Finally the samples were allowed to cool slowly to 200°C.

A Scanning Electron Microscope (SEM) was used to examine the morphology of the composite system. Three kinds of grains are observed: (1) Large grains (1 to 5 microns) with sharp edges and smooth facet formation (identified as $Y_1Ba_2Cu_3O_{7-\delta}$); (2) Large grains (also about 5 microns) with rounded corners (identified as copper); and (3) Very small grains (less than 1000 Å) between the above two types of large grains (identified as silver). The identification of these grains was based on Energy Dispersive Spectroscopy (EDS).

Powder X-ray diffraction measurements (using a copper K_α radiation wavelength of 1.5409 Å) were performed to examine the crystal structure of samples. The characteristic lines of copper oxide (CuO) at $2\theta = 35.6°$, 38.8°, and 48.8° were found and the characteristic lines at $2\theta = 43.4°$, 50.9°, 74.5°, and 90.2° for metallic copper were not observed. The metallic copper powder oxidized during the sintering process but the superconductivity in $Y_1Ba_2Cu_3O_{7-\delta}$ was preserved.

The composite samples were further studied by their electrical resistivity and mechanical strength. The normal state resistivity of the composites is smaller than that of the ceramic $Y_1Ba_2Cu_3O_{7-\delta}$ superconductor by a factor of 3 or more. The superconducting transition temperatures (zero resistance) were between 86 K and 87 K.

The composites had much better mechanical properties than the ceramic $Y_1Ba_2Cu_3O_{7-\delta}$. They could be machined into any desired shape and for instance, we made a nut and bolt pair that was still superconducting and threaded nicely together. To our knowledge, no one has reported such mechanical properties for ceramic superconductors. We also performed pressure tests on our samples. The pure ceramic $Y_1Ba_2Cu_3O_{7-\delta}$ sample broke at an uniaxial pressure of 8 Kpsi while our composite samples did not break up to 70 kpsi or even higher.

III.B. Bulk $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ (n=2 and 3) materials.

III.B.1 Fabrication

The samples were prepared by a multi-step process. In the first step, a precursor made of $Ba_2Ca_2Cu_3O_7$ was prepared by the solid state reaction technique. Raw powders of $BaCO_3$, $CaCO_3$, and CuO were thoroughly mixed to produce a 2 : 2 : 3 stoichiometry. The mixture was sintered in air at 940°C for 48 hours with an intermediate grinding. The second step was to incorporate thallium into the precursor. Tl_2O_3 powder was mixed with the precursor according to a 1.1 : 1 ratio (to account for the loss of thallium) and the mixture was pressed into pellet form under a pressure of 40 Kpsi. The pellets were wrapped in gold foil and loaded in a quartz tube with both ends open to allow gas exchange. The whole assembly of pellets and quartz tube was instantly inserted into a furnace preheated to 900°C with oxygen flowing and held at that temperature for 10 minutes. This was followed by furnace cooling to 200°C. In the third step, pellets from the previous two steps were ground up, re-pressed, and re-sintered at 900°C in flowing oxygen for 4 hours. Then they were slowly cooled to 600°C and held at that temperature in flowing oxygen for 12 hours. Finally the samples were furnace cooled to room temperature.

III.B.2 Sample characterization

The crystal structure of the samples was determined by X-ray powder diffraction measurements. There were essentially no impurity phases and we were able to index the spectrum lines to a tetragonal structure. The d-spacings of these lines were determined from the diffraction pattern and a least squares fit was used to calculate the lattice constants. The results are a = 3.8416 ± 0.0009 Å and c = 35.347 ± 0.070 Å. Compared with previously reported results, our lattice constant a is in reasonable agreement with others' work while lattice constant c is slightly smaller than others. This may possibly be related to our prolonged oxygen annealing procedure (step 3 of sample preparation) during which more oxygen could be incorporated into the system, leading to a contracted c axis.

The electrical resistivity as a function of temperature was measured using a standard dc four probe technique. The magnitude of the measuring current was 1mA. The superconducting transition starts at 125 K and the zero resistance state is achieved at 119 K. The normal state resistivity is slightly higher than that of good $Y_1Ba_2Cu_3O_{7-\delta}$ samples but it is 2 to 5 times smaller than that of $Tl_2Ba_2Ca_2Cu_3O_{10}$ samples which did not go through step 3 of the above process.

The electrical leads for the noise power measurement were connected to samples with silver. Pads of silver, 2000 Å thick, were evaporated onto the two end faces (2 mm x 8 mm) of each rectangular pellet for current contacts and onto two circular areas (about 0.5 mm in diameter and 13 mm apart) for voltage contacts on a third side. The samples after evaporation were annealed in oxygen at 500°C for 1 hour. Then thin copper wires were attached to the silver pads by means of silver epoxy. The resulting contact resistance at each point is less than 15 mΩ by this technique.

III.C. $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals

The $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals used were prepared by a melt-growth process. A mixture with a formula of $Y_1Ba_4Cu_{10}O_{16}$ was first obtained by thoroughly mixing Y_2O_3, $BaCO_3$, and CuO together. The mixture (loaded in an alumina crucible) was heated to 1025°C in air for 4 hours and then slowly (2°C/h) cooled to 900°C, followed by a faster cooling (50°C/h) to room temperature. The crystal geometry was that of a thin plate with an average size of 2 mm x 2 mm x 0.1 mm. An energy dispersive analysis was conducted on a scanning electron microscope to obtain elemental information about the crystals. The atomic ratio was found to be close to Y:Ba:Cu = 1:2:3, which assured us that they were indeed $Y_1Ba_2Cu_3O_{7-\delta}$ crystals. The crystals were annealed at 500°C in flowing oxygen for 1 to 7 days to increase their oxygen content. The electrical resistance as a function of temperature was measured using the standard dc four probe technique. We prepared both superconducting and non-superconducting single crystals, the difference being the different oxygen content in these crystals. In the single crystals, the superconducting transition starts at

86 K and zero resistance is achieved at T_c = 80 K. The observed width (6 K) of the superconducting transition region is due to the small oxygen deficiency.

IV. Experimental results on 1/f noise

IV.A Bulk $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ (n=2 and 3)

The spectra of our measurements can be fitted to $S_v(f) = Af^{-\alpha}$, and the 1/f noise exponent $\alpha(T)$ is1.08±0.10 for all measurements, falling well into the accepted 1/f noise range. The current dependence of the 1/f noise spectral density $S_I(f)$ has the expected I^2 dependence for 100 mA < I < 260 mA.

The 1/f noise of copper oxide superconductors in the normal state is very large. Quantitatively we can use the Voss-Clarke temperature fluctuation model [1] that has had some success in explaining the 1/f noise behavior of a certain group of superconductors in the superconducting transition region. This model predicts the following equation for the 1/f noise power spectral density:

$$S_v(f) = V^2\beta^2 k_B T^2/fC_vA \qquad (2)$$

where $\beta = (1/R)dR/dT$ is the temperature coefficient of resistance, k_B the Boltzmann constant, C_v the heat capacity, and A a geometric factor of order unity. Using published specific heat data for $Tl_2Ba_2Ca_1Cu_2O_8$ [2] and our resistivity data, we can compare the quantity S_v/V^2 calculated from equation (2) with experimentally measured data on our samples. The difference in the magnitude of experimental data and calculated results is as large as eight orders of magnitude. The large 1/f noise power from our experiments is comparable to that obtained on $R_1Ba_2Cu_3O_{7-\delta}$ (R = Y or Er) systems, which has been shown to be approximately ten orders of magnitude larger than that suggested by conventional models.

The 1/f noise power decreases with decreasing temperature, even though this temperature dependence is relatively weak. In many samples,

tremendous peaks of enhanced noise power (spanning at least three orders of magnitude) are found in the superconducting transition region. These peaks have been previously observed in $R_1Ba_2Cu_3O_{7-\delta}$ (R = Y or Er) systems and in Bi-Sr-Ca-Cu-O system. In some good quality samples, however, these peaks are reduced or even totally disappear in the superconducting transition region. To our best knowledge, this is the first observation of the absence of enhanced 1/f noise spectral density in copper oxide superconductors in the superconducting transition region.

We have observed no correlation between resistivity, normal state 1/f noise spectral density, and the behavior of 1/f noise in the superconducting transition region. This seems to suggest that: (i) the spectral density of 1/f noise in the normal state does not directly depend on sample quality (such as resistivity, T_c, and structural characteristics such as the weak link nature); and (ii) the 1/f noise in the normal state and in the superconducting transition region comes from different origins.

In summary, our experiments on bulk $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ materials lead to the following results:
(i) noise level in the normal state is about 8 to 10 orders of magnitude higher than that of conventional metals;
(ii) no correlation is observed between sample quality that we have identified (e.g., resistivity, T_c, and structural characteristics) and the magnitude of the noise spectral density in the normal state. Therefore the source of noise in the normal state has not been identified.
(iii) The temperature dependence is essentially the same in all samples, increasing with increasing temperature.
(iv) The enhancement of the 1/f noise in the superconducting transition region exists in many samples but it is reduced or even totally disappears in some of our good quality samples.

IV.B. $Y_1Ba_2Cu_3O_{7-\delta}$ thin films

The films used for this study were obtained from Superconductive Components, Inc. (Columbus, Ohio). The results of 1/f noise measurements on $Y_1Ba_2Cu_3O_{7-\delta}$ thin films show that the normalized spectral density S_V/V^2 of the 1/f noise in the normal state has a large amplitude. A simple

way of quantitatively comparing its amplitude with that of conventional materials such as metals is to use Hooge' empirical formula [3]: $S_v = \gamma V^2/N_c f$ where N_c is the total number of charge carriers in the sample and γ is in the range of 10^{-1} to 10^{-5} for most metals. N_c can be easily calculated from charge carriers density (2×10^{21} cm^{-3}) [4] and the sample volume. Our data show that the numerical value of γ is 4.4×10^4 at 300 K for our sample. Therefore the amplitude of γ in our thin film sample is at least 5 orders of magnitude larger than that in most metals. We propose that the large amplitude of the noise spectral density is due to potential fluctuations in the grain boundary area. The detailed discussion will be given in section IV.

The 1/f noise spectral density decreases weakly with decreasing temperature. There are tremendous peaks of enhanced noise power of the sample, located in the superconducting transition region. These peaks have been previously observed in bulk $Y_1Ba_2Cu_3O_{7-\delta}$ systems, single crystal Bi-Sr-Ca-Cu-O system, and bulk Tl-Ba-Ca-Cu-O system. The nature of these giant 1/f noise peaks in the superconducting transition region has not been well identified even though a number of speculations have been made, including the effect of large resistance fluctuations in the superconducting transition region [5], magnetic flux noise [6], as well as the influence of microstructures [7].

In summary, our experiments on $Y_1Ba_2Cu_3O_{7-\delta}$ thin films show the following results:
(i) noise level in the normal state is at least 5 orders of magnitude higher than that of conventional metals;
(ii) The noise spectral density decreases weakly with decreasing temperature.
(iii) There exists pronounced enhancement of the 1/f noise in the superconducting transition region.

IV.C. $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals

We have performed 1/f noise measurements on many single crystals that have very different resistance characteristics. Some crystals have a "metallic" resistance that decreases with decreasing temperature at all

temperatures. When the superconducting transition temperature Tc is approached, the resistance becomes zero. Some other samples have a "semiconductor" resistance that decreases initially with decreasing temperature and below 170 K the resistance starts to increase. The change of the resistance behavior is known to be a result of large oxygen deficiency. There is no superconducting transition observed above 77 K, due to the insufficient oxygen content in these samples.

The dc probing current (10 - 80 mA) was passed through the a-b plane of the sample. The noise spectra of our samples can be fitted to $S_V(f) = Af^{-\alpha}$, with the noise exponent $\alpha(T) = 1.06 \pm 0.10$ for the measured temperature range. The current (I) dependence of the noise spectra has the expected I^2 dependence. All noise spectra have characteristic 1/f behavior. Several observations can be made from our data.

A. The magnitude of the 1/f noise spectral density of our $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals is much larger than that of conventional materials. We consider Hooge's empirical formula [3]: $S_v = \gamma V^2/N_c f$ where N_c is the total number of charge carriers in the sample and γ is in the range of 10^{-1} to 10^{-5} for most metals. N_c can be calculated from the charge carrier density n_c (2×10^{21} cm^{-3}) [12] and sample volume Ω (listed in Table I). Our data show that at T = 295 K the numerical values of γ larger than 2×10^3 for our crystals. Therefore the values of γ in $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals are at least 4 orders of magnitude larger than that found in most metals.

B. The magnitude of S_v/V^2 of samples A and B both decreases with decreasing temperature. This behavior appears to be uncorrelated with the temperature dependence of the resistivity data. The lack of correlation between the temperature dependence of S_v/V^2 and the resistivity suggests that the major contributions to the 1/f noise and the resistivity have different origins.

C. In samples that have the superconducting transition, we were unable to observe enhanced 1/f noise in the superconducting transition region. We carried out measurements very close to T_c in the transition region until we could not observe 1/f noise. We observed no enhancement of the 1/f noise spectral density. This absence of enhanced 1/f noise in the

superconducting transition region in $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals is much different from the behavior in bulk $Y_1Ba_2Cu_3O_{7-\delta}$ materials where greatly enhanced 1/f noise spectral density has always been observed.

Experiments have indicated that even in the single crystal form, copper oxides are still composed of domains separated by domain walls or internal junctions [8]. The presence of these domains or subgrains in single crystals is a direct result of extensive crystallographic defects such as stacking faults and twin boundaries [9] in copper oxides. In section IV, we will discuss possible explanations of the large amplitude of the noise spectral density observed from our experiments.

In summary, our 1/f noise measurements on $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals have led to the following observations:
(i) the normalized noise spectral density S_v/V^2 of the single crystals is at least 4 orders of magnitude larger than that of metals;
(ii) the temperature dependence of S_v/V^2 is independent of resistivity characteristics;
(iii) in the superconducting transition region, there is no anomalously enhanced 1/f noise as seen in bulk and thin film copper oxide systems.

In experiments following the termination of this contract, we were successful in observing 1/f noise for a probing current in the a-b plane and also for a probing current in the c direction. This is the first observation of the noise in the c direction of single crystals and represented a technically difficult experiment. In the superconducting transition region, there was a large 1/f noise peak for measurements along the c direction but not in the a-b plane. Based on this observation, we have a much clearer understanding of the source of 1/f noise in the transition region. The source is the melting of the vortex lattice and is the subject of another manuscript, a preprint of which is attached.

IV.D. $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ thin films

These films were obtained from Superconductor Technology, Inc. The noise voltage fluctuation spectrum (S_v) of the $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ thin

films can be fitted to

$$S_V(f) = Af^{-\alpha},$$

with the noise exponent $\alpha(T) = 1.10 \pm 0.15$ for the measured temperature range (from T_c , which is about 100 K, to 300 K). The current (I) dependence of the noise spectra has the expected I^2 dependence. At each temperature the noise spectrum was measured from 0.1 Hz to 100 Hz with a frequency increment of 0.125 Hz.

We first examine the magnitude of the normalized spectral density, S_V/V^2, in the normal state ($T >> T_c$). A simple way of quantitatively analyzing the data is to use Hooge' empirical formula [3]: $S_V = \gamma V^2/N_c f$. The total number of charge carries in the sample, N_c, can be calculated from the carrier density (2×10^{21} cm^{-3}) [10] and the sample volume. Our data show that the numerical value of γ is 0.5 - 2 at 300 K for our Tl films which is close to that of metals and much smaller than that observed in other copper oxide materials. It has been suggested that large 1/f noise observed in copper oxide materials is related to various structural defects such as grain boundaries and twinning structures in these materials. Our Tl films are essentially free from twinning structures but there still exist many grain boundaries. If the grain boundaries are thin enough (< 10 Å), however, it is possible to use the structural defect related noise model to demonstrate that the noise generated from the grain boundaries are much reduced.

The second feature of our data is that there exists the enhancement of S_V/V^2 in the superconducting transition region in some thin film samples (close to 5 orders of magnitude). But it is greatly reduced in some other samples (less than 1 order of magnitude). The samples with large reduction of S_V/V^2 in the superconducting transition region have better c-axis alignment as indicated by X-ray diffraction rocking curve data. In our 1/f noise experiments performed in the a-b planes of $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals, no enhancement of 1/f noise in the superconducting transition region was observed. This observation is consistent with our present results obtained on Tl films. Since 1/f noise in the superconducting transition region is generally associated with magnetic flux motion, our

experimental data suggest that there is a close correlation between the flux motion and the crystal structure of copper oxide superconductors.

In summary, our measurements of 1/f noise on $Tl_2Ba_2Ca_1Cu_2O_8$ thin films show the following results:
(i) The magnitude of S_v/V^2 for our samples in the normal state is much lower than that previously observed in other copper oxide materials and is comparable with that of conventional metals.
(ii) In the superconducting transition region the enhancement of 1/f noise is greatly reduced in some highly c-axis aligned films.

We attribute these observations to the unique crystal structure of the $Tl_2Ba_2Ca_1Cu_2O_8$ thin films. Our data suggest that the noisy behavior previously observed in many copper oxide superconductors is not an intrinsic property of these materials.

V. Model calculations

V.A. Basis of the Model

Because of their ceramic nature, all bulk and thin film copper oxide materials are composed of small grains (on the order of a few microns) separated by grain boundaries. This "composite" picture applies even to single crystals because of twinning and other crystal defects. In this sense the difference between bulk, thin film, and single crystal systems is the different spatial scale of the structural defects. The defects can be (i) grain boundaries in bulk and film materials; (ii) domain boundaries inside individual grains; and (iii) twinning boundaries or other crystal defects in single crystals and thin films.

We assume that the "defect regions" have a metal-insulator-metal (MIM) structure and there is an energy barrier for charge carriers to overcome in the insulating (or possibly semiconducting) layer. These insulating layers are very thin ($\approx$ 10 Å) and the predominant conduction mechanism is a tunneling process in these junctions [11]. When charge carriers are trapped in the junctions, the height of the energy barrier is changed. Fluctuations in the number of trapped charge carriers lead to fluctuations

in the barrier height, which in turn gives rise to fluctuations in conductance. This model is a direct application of McWhorter's potential fluctuation mechanism [12].

We start with the spectral density $S_N(f)$ of quantity N, the number of trapped charge carriers. We make the following assumptions [13] about the energy E and the characteristic time constant τ: (1) there is a uniform distribution of E; (2) τ and E are related by $\tau = \tau_0 \exp(E/kT)$ where k is the Boltzmann constant; and (3) there are two cutoff frequencies $1/\tau_1$ and $1/\tau_2$ such that $1/\tau_2 << f << 1/\tau_1$. Under these assumptions we may obtain:

$$S_N(f) = \frac{N}{\ln(\frac{\tau_2}{\tau_1})} \frac{\pi}{2f} \qquad (1)$$

The tunneling current density $J(\mathcal{V},T)$ in a junction of spatial thickness s at junction voltage V and temperature T is given by [14]:

$$J(\mathcal{V},T) = \frac{4\pi me}{h^3B^2} \frac{\pi BkT}{\sin(\pi BkT)} [1-\exp(-Be\mathcal{V})] \exp(-A\psi^{1/2}) \qquad (2)$$

where m = electron mass, e = electron charge, h = Planck constant, ψ = barrier height, $A = 4\pi s(2m)^{1/2}/h$, and $B=2\pi s(2m/\psi)^{1/2}/h$. The tunneling conductance $g = dI/d\mathcal{V}$ can then be derived easily from equation (2) and this conductance is a function of barrier height ψ. The noise spectral density $S_g(f)$ of the conductance fluctuations in one junction is determined by fluctuations in the number of trapped charge carriers and their consequent effect on the conduction due to fluctuations of the height of the energy barrier.

$$S_g(f) = \left(\frac{dg}{d\psi} \frac{d\psi}{dN}\right)^2 S_N(f) \qquad (3)$$

The calculation of $dg/d\psi$ is straightforward from equation (2) while the derivation of $d\psi/dN$ involves the Fermi distribution of charge carriers and the potential shifts introduced by these charge carriers. Under the assumptions that (1) the potential barrier height in each junction

fluctuates independently and (2) the junctions are located on parallel chains in the direction of the macroscopic current, we may obtain [15] (neglecting conduction between the chains) $S_v(f)/V^2 = (\Omega_0/\Omega)S_g(f)/g^2$ and the final normalized 1/f noise spectral density of voltage fluctuations for the whole sample is:

$$\frac{S_V(f)}{V^2} = \frac{\pi^5 m e^4}{h^2} \frac{s^4 l}{wt\varepsilon^2\psi} \left[1 - \frac{\pi kT}{2\psi} \frac{\cos(\pi kBT)}{\sin(\pi kBT)}\right]^2 \frac{N}{\Omega \ln(\frac{\tau_2}{\tau_1})} \frac{1}{f} \qquad (4)$$

where w, t = spatial lateral dimensions of the junction, = spatial longitudinal dimension of the junction, Ω_0 = lwt, the volume of one junction, Ω = the sample volume, and N = number of trapped charge carriers in one junction (which is related to the trapped charge carrier density n by N = ntws).

V.B. Discussion

We briefly discuss some predictions that one can make based on equation (4). First of all, $S_v(f)/V^2$ is inversely proportional to both sample volume and frequency, which is generally expected for 1/f phenomenon. Secondly, it is very sensitive to the spatial thickness s of the tunneling barrier. Reducing the thickness by a small fraction may result in a very large suppression of the spectral density amplitude because of the s^4 dependence and the effect of s on parameter B. On the other hand one does not expect to see the amplitude of 1/f noise spectral density increase indefinitely with s because when s becomes sufficiently large the dominant conduction mechanism in the junction area is no longer tunneling and our analysis here will not be valid. Finally, it is easy to demonstrate graphically that the spectrum predicted by equation (4) with our typical parameters is a slow varying function of temperature that decreases with decreasing temperature. The rate of change with temperature depends on the numerical values of s and ψ.

V.C. Comparison with experiments

Equation (4) has been used to calculate the 1/f noise spectral density and

a quantitative agreement between calculation and experimental data is achieved.

In calculations, the thickness of the insulating layer in the MIM structure is determined by the grain boundaries in the bulk and thin film samples or by the twinning boundaries in the single crystal samples. We do not have direct information on the barrier characteristics such as barrier thickness s, barrier height ψ, and density of occupied states of trapped charge carriers n. Therefore we use them as adjustable parameters in the calculation. Some typical fitting parameters are listed in Table I.

At this point we have not performed direct experimental test on barrier characteristics (barrier thickness, barrier height, number of trapped charge carriers, and assumed simple rectangular barrier shape). However, the good agreement between experimental results and calculation together with reasonable numerical values of the fitted parameters certainly suggest the validity of our proposed model.

VI. Conclusions

We have performed 1/f noise measurements on a large number of samples, including $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ in the bulk (n=2 and 3) and thin film (n=2) form, $Y_1Ba_2Cu_3O_{7-\delta}$ in the thin film and single crystal form. We obtain 1/f noise spectral densities with very large amplitudes (except in the $Tl_2Ba_2Ca_1Cu_2O_8$ thin films) in the normal state of these materials. In order to explain this observation, we propose a model of MIM junctions for copper oxide materials in their normal state. Our calculations agree quantitatively with experimental results. The 1/f noise spectral densities obtained on $Tl_2Ba_2Ca_1Cu_2O_8$ thin films have low amplitudes that are comparable with that of metals. These data further support the point of view that the noisy behavior observed previously in copper oxide materials is largely due to various structural defects. This noisy behavior is not an intrinsic property of these materials.

We also observe interesting correlations between the crystal structure and the behavior of the 1/f noise in the superconducting transition region. In all bulk materials and in thin film $Y_1Ba_2Cu_3O_{7-\delta}$ samples, there exist

enormously enhanced 1/f noise spectral densities (typically 4 to 5 orders of magnitude). In highly c-axis aligned $Tl_2Ba_2Ca_1Cu_2O_8$ thin films, however, the enhancement of the 1/f noise spectral densities is much reduced to less than 1 order of magnitude. When the probing current is in the a-b plane of $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals, this enhancement totally disappears, consistent with the results obtained on $Tl_2Ba_2Ca_1Cu_2O_8$ thin films. When the probing current is along the c-axis, the large peak in the transition is observed. The anisotropy in the 1/f noise explains why such a peak is always seen in bulk materials. **The source of 1/f noise in this region is the freezing (or melting) of the vortex lattice.**

Table I. Fitting parameters used to calculate the 1/f noise spectrum from equation (4). Samples A and B are $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals. Sample C is a $Y_1Ba_2Cu_3O_{7-\delta}$ thin film sample.

Sample	A	B	C
s	11.0 Å	10.5 Å	12.0
l	1000 Å	1000 Å	3.0 μm
t	15 μm	15 μm	4000 Å
w	15 μm	15 μm	3.0 μm
Ω	1.0×10^{-5} cm^3	3.0×10^{-5} cm^3	3.89×10^{-6} cm^3
ψ	0.040 eV	0.055 eV	0.07 eV
n	2.0×10^{20} cm^{-3}	1.8×10^{20} cm^{-3}	2.8×10^{19} cm^{-3}

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Appendix. Publications Resulting from ONR Grant N00014-88-K-0413

1. "Superconducting (YBaCuO)-(CuO)-Ag composites", Yi Song, Yue Cao, Anupam Misra, and J. R. Gaines, Journal of Materials Research, 4, 802 (1989)

2. "Oxygen diffusion in $Y_1Ba_2Cu_3O_{7-\delta}$ grains: An experimental study of ozone and oxygen annealing processes", Yi Song, Xiao-Dong Chen, James R. Gaines, and John W. Gilje, Journal of Materials Research, 5, 27 (1990)

3. "1/f noise power measurements of $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ (n=2 and 3)", Yi Song, Anupam Misra, Yue Cao, Antonio Querubin, Jr., Xiao-Dong Chen, Peter P. Crooker, and James R. Gaines, Physica C, 172, 1 (1990)

4. "1/f noise and morphology of $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals", Yi Song, Anupam Misra, P.P. Crooker, and James. R. Gaines, Physical Review Letters, 66, 825 (1991)

5. "The conductivity threshold for superconductivity in copper oxides: effect of localization and strong correlations", Yi Song and James R. Gaines, submitted to Journal of Physics: Condensed Matter.

6. "1/f noise in $Tl_2Ba_2Ca_1Cu_2O_8$ thin films", Anupam Misra, Yi Song, P. P. Crooker, James R. Gaines, and Albert H. Cardona, accepted for publication by Applied Physics Letters.

7. One manuscript is in preprint form. "Anisotropic 1/f Noise and Motion of Magnetic Vortices in $Y_1Ba_2Cu_3O_{7-\delta}$ ", Yi Song, Anupam Misra, P.P. Crooker, and James. R. Gaines.

PATENT REPORT

No patents were applied for under this contract. Nor are any anticipated based on the work of this contract.